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Synthesis Characterization and Morphology of a Cis 1,4 Polyisoprene/Poly n-butylmethacrylate Diblock Copolymer.

by

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Cambridge, MA 02139

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Homogeneous anionic polymerization methods were employed to synthesize a diblock copolymer of the form $[A]_n$-b-$[B]_m$ in which repeat unit A is isoprene, B is n-butylmethacrylate and b is a single unit of 1,1 diphenylethylene. Various physical-chemical characterization methods were employed to determine that the molecular weights of the A and B blocks are 80,000 and 160,000 g/mole respectively. NMR spectra indicated that the poly n-butylmethacrylate moiety is composed predominantly of syndiotactic triads. Thermal analysis and dynamic mechanical testing were used to determine the polyisoprene and poly n-butylmethacrylate glass

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transition temperatures, which were around -70° and 20° C respectively; the poly n-butylmethacrylate transition observed in the viscoelastic experiments was unusually broad, covering more than 75° C from onset to completion. Thin films of the diblock copolymer prepared by solvent evaporation casting methods, using a variety of solvents and a wide range of solvent evaporation rates, showed a variety of morphologies in transmission electron micrographs. Most notable among these was a structure obtained in rapid-evaporation castings which contained relatively large regions of homogeneous diblock copolymer embedded in the microphase-separated material. While these homogenized regions remain unchanged indefinitely in the bulk material at room temperature, they tend to decompose to the stable microphase-separated material upon heating or upon addition of solvent.

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In a previous series of papers from our laboratory (1-4) we have reported on the structure and properties of various elastomer blends. Particular emphasis was given to the ternary system of 1,4 polybutadiene, cis 1,4 polyisoprene, and a corresponding diblock copolymer of the two. For that particular case, the diblock copolymers were homogeneous materials (2) while the corresponding homopolymers formed heterogeneous blends (1,3). In certain proportions the diblocks provided a homogenizing effect in the ternary blends (1,3).

In view of the results cited above, it was of interest to investigate the possibilities for obtaining a diblock copolymer in which both segments were rubbery but whose repeat units had very different structures. Of the various systems considered (5) a variety of reasons led to the choice of n-butyl methacrylate and isoprene for the two monomers. Although poly n-butylmethacrylate is not strictly rubbery at room temperature, its reported (6) glass transition temperature of about 20° C indicates that rubbery behavior will be observed at moderately elevated temperatures. Although various methacrylates have been polymerized using anionic polymerication methods (7,8) and block copolymers of isoprene and methylmethacrylate have been reported (9), there is no information available on diblock copolymers of cis 1,4 polyisoprene and poly n-butylmethacrylate.

The present paper describes the synthesis methods used to obtain relatively large quantities (~50 grams) of the desired diblock copolymer. Results of various chemical, mechanical and morphological characterization experiments are also reported. Particular attention will be given

to the variety of non-equilibrium morphologies which can be obtained with this copolymer.

Synthesis

Purification and Handling of Materials: Solvents used in the polymerization were n-hexane and tetrahydrofuran (THF). These were each double-distilled under argon in the presence of small amounts of benzophenone, potassium and sodium. Because THF absorbs trace amounts of water readily, another purification step was needed for this solvent just before use; a small amount of 0.25 molar sodium naphthylene-THF solution was injected into the distilled THF until a light green color (10) persisted, at which point the desired volume of solvent was introduced to the reaction vessel.

Isoprene monomer (Aldrich Chemical) was refluxed over sodium wire in an argon atmosphere until a light blue color was observed. A center fraction was collected, degassed and vacuum distilled over fresh sodium into a delivery buret. The n-butylmethacrylate monomer (Polysciences) contained 25 ppm hydroquinone inhibitor which was removed by successive washings with sodium hydroxide solutions and distilled water. After drying over molecular sieves at 0° C, the uninhibited monomer was refluxed at 51° C over boric acid to remove alcohol impurities (11). A central fraction was stored over molecular sieves; this fraction was redistilled at 51° C, cooled, and degassed immediately prior to polymerization.

Secondary butyllithium (1.4 molar in cyclohexane as received from

Aldrich Chemical) was used as the initiator. The stock initiator solution was diluted with cyclohexane and titrated using the method of Eppley and Dixon (12); quantitative delivery to the reactor was accomplished using an adaptation of the method of Rempp and Lutz (13).

Polymerization: In order to isolate the reactor from terminating impurities such as oxygen or water in the atmosphere, a small overpressure of highly purified argon was maintained in the reactor throughout the polymerization. Synthesis of the diblock copolymer involved the sequential reaction of the two monomers under appropriate conditions for each. The cis 1,4 polyisoprene segment was synthesized first in hexane. Reaction temperatures was 50 to 55° C.

We found that a small amount of an intermediate monomer was necessary to initiate a successful block copolymerization of n-butylmethacrylate monomer with the living polyisoprene anions. Freyss et al (14) have shown that small amounts of 1,1 diphenylene (DPE) eliminated side reactions with the ester functionality of methyl methacrylate monomer in lithium catalyzed anionic polymerizations. This same compound (DPE) proved to be useful in suppressing these side reactions for the butyl methacrylate monomer used here. Following the addition of DPE (about 3-fold greater than the stoichiometric ratio), the reaction medium was cooled to -70° C and the purified THF was added. Finally the n-butylmethacrylate monomer was dripped slowly into the reaction medium and

the second block polymerization was carried out at -70° C. The reaction was terminated with methanol and the polymer was precipitated in methanol containing 1 gram/liter of an antioxidant (Antiox 330, Ethyl Corp.). The recovered copolymer was vacuum dried and a yield of about 99% was obtained.

Molecular Characterization

Gel permeation chromatography experiments were carried out on a Waters Model 200 GPC equipped with four styrogel columns (10^6Å - 10^3Å) and a differential refractive index detector. Toluene solutions of 1 to 2 grams per liter were used; the flow rate was 1 ml/minute and the temperature 25° C.

A GPC trace was obtained for the sample of the polyisoprene block taken from the reactor prior to the subsequent initiation of the poly n butylmethacrylate block. Using standard universal calibration methods (15,16), and available data (17,18) on the Mark-Houwink parameters for polyisoprene and the reference polymer, in this case polystyrene, the number average molecular weight and polydispersity index were calculated. The polydispersity values reported here have been corrected for axial dispersion according to the method of Balke and Hamilec (19). Results are given in Table 1. The validity of the calibration methods and correction factors was checked and verified by conducting osmometry experiments on several samples of similarly prepared polyisoprene.

GPC experiments were also conducted on a homopolymer of n-butylmethacrylate prepared using methods and materials (including the 1,1

diphenylethylene precursor) which were identical to those described above. In this case toluene was not a good solvent for the GPC experiment owing to the small (and negative) signal from the differential refractometer for the toluene-poly n butylmethacrylate system. A GPC trace obtained from a poly n butylmethacrylate-THF solution is shown in Figure 1. A single narrow peak is observed; thus the combined steps of adding a 1,1 diphenylethylene precursor and the polar solvent THF appear to have suppressed the tendency toward a bimodal distribution of molecular weights that has been reported for the lithium catalyzed anionic polymerization of polar monomers in nonpolar solvents (14,20).

Molecular characterization of the diblock copolymer required several complimentary experiments. Particular attention was given to the determination of the amount of homopolyisoprene which is present in the diblock sample owing to the inevitable termination of some of the living polyisoprene anions during the course of the first stages of the synthesis. The number average molecular weight of the diblock estimated by osmometry (Table 1) agrees well with the value calculated from stoichiometry, indicating that the amount of isoprene homopolymer is small. A more quantitative estimate of homopolyisoprene content was obtained using the results of intrinsic viscosity measurements conducted at 30° C in toluene and the method of data reduction developed by Prud'Homme and coworkers (21). Using this method it was estimated that terminated polyisoprene homopolymer constituted about 8 wt % of the total product obtained from the diblock synthesis.

Carbon-13 NMR characterization of the poly n butylmethacrylate moiety of the diblock and of a homopolymer prepared under similar conditions indicated that there was a high degree of syndiotactic addition. The percentage of syndiotactic, heterotactic and isotactic triads was 75.0(±1.6), 22.9(±0.5) and 2.2(±1.7) respectively. Triad information was obtained from independent determinations based on the carbonyl and the methine carbon atoms. Degrees of tacticity based on dyads were obtained from the methylene carbon of the chain backbone; results were 83.9% syndiotactic dyads and 16.1% isotactic dyads. Comparison of the dyad and triad information indicated that the propagation step in the butyl methacrylate synthesis is well described by Bernoullian statistics.

Characteristics of Solvent Cast Films

Various methods were employed in the production of thin films for morphology examination and physical properties testing. Solutions of about 5% (by weight) diblock copolymer in the selected solvent or solvent mixture were subjected to two different casting procedures. One method (1,22) involves slow solvent evaporation over the period of many days with the polymer film being deposited onto a mercury surface; the second method is a rapid spin-casting technique (22,23) in which the solvent evaporation takes place over the period of a few hours.

The solvents employed in the casting of films were benzene, toluene, methylene chloride and two solvent mixtures: 80% benzene/20% 2-pentanone and 80% n hexane/20% methylene chloride. Benzene, is a good solvent for both blocks of the copolymer while 2-pentanone is essentially a selective solvent for the n-butylmethacrylate block. The relative volatility of benzene compared to 2-pentanone at room temperature is about 10:1; thus, as solvent evaporation proceeds from the ternary mixture of benzene, 2-pentanone and the polyisoprene/poly n butylmethacrylate diblock, a premature precipitation of the polyisoprene blocks is expected. On the other hand in the methylene chloride/n hexane solvent system, selective precipitation of the poly n butylmethacrylate is expected.

Specimens for electron microscopy were obtained according to the following procedures. Pieces of the cast films were stained by exposure (24) to osmium tetroxide for 6 days. Thin (ca 1000 Å) sections were obtained using an LKB Ultratome III microtome fitted with a diamond knife. The sections were mounted on 200 mesh copper grids and micrographs were obtained on a Phillips 200 electron microscope using an accelerating voltage of 80 kV. Representative results for slow-cast films are presented in Figure 2 in which polyisoprene appears as the darker regions in every case. Figure 3 shows the morphologies obtained for films cast from various solvents using the rapid evaporation method of sample preparation. The most striking feature is the presence of relatively large regions of material embedded in the microphse-separated block copolymer. These regions are also stained by the osmium tetroxide treatment indicating that some isoprene units must be present.

Transition temperatures characteristic of the contituents of the diblock copolymer were determined on a DuPont 900 Thermal Analyzer in the DTA (Differential Thermal Analysis) and TMA (Thermomechanical Analysis) modes. Heating rates were always between 5 and 15° C/min. For the sample formed by slow evaporation from benzene/pentanone, glass transitions were observed in DTA at -73° C and 17° C corresponding to the polyisoprene and poly n-butylmethacrylate phases respectively. In the TMA mode two separate probes were used. The blunt-end expansion probe revealed a clear transition at -69° C and 16° C. Using the penetration probe, the lower temperature transition also appeared at -69° C but a marked softening of the sample beginning near -40° C resulted in sufficiently rapid penetration to mask the onset of the upper transition.

Transition temperatures were also determined in 3.5 Hz forced oscillation linear viscoelastic experiments conducted on a Rheovibron DDV-II apparatus using specimen mounting procedures and correction factors required for the tensile geometry used in these experiments (4,25). Results are shown in Figure 4. The location of the polyisoprene transition (identified as an inflection in the storage modulus curve or a peak in the loss tangent) around -65° C is reasonably consistent with the results of DTA and TMA. The transition temperature of the butyl methacrylate phase is poorly defined in these dynamic mechanical data. The second decrease in the storage modulus begins to occur at temperatures below 0° C and the inflection on the storage modulus curve appears near 40° C. Similarly tan δ begins to rise immediately after the polyisoprene transition is complete and peaks near 50° C, well above the transition temperature

observed in the thermal analysis experiments. Dynamic mechanical tests on a similarly prepared poly n-butylmethacrylate homopolymer revealed a broad viscoelastic relaxation which was essentially identical to the upper transition shown in Figure 4.

Discussion

The successful synthesis of the polyisoprene/poly n-butylmethacrylate diblock required the use of the intermediate, 1,1 diphenylethylene, whose major function was to reduce the reactivity of the polyisoprene anions so that smooth polymerization of the n-butylmethacrylate would result. The criteria upon which the choice of DPE was based were (i) living polyisoprene chains initiate DPE (ii) DPE does not homopolymerize under the conditions present in the reactor (iii) living DPE initiates n-butylmethacrylate. Such intermediate units are thus very useful for facilitating the construction of polymeric molecules which would otherwise be unattainable.

The bulk morphology of the polyisoprene/poly n-butylmethacrylate diblock is sensitive to the nature of the solvent from which it is cast and unusually sensitive to the rate of solvent evaporation. The slow-cast morphologies shown in Figure 2 vary from well-formed polyisoprene spheres in a poly n-butylmethacrylate matrix (benzene/pentanone castings) to long polyisoprene rods (benzene) to a co-continuous morphology (methylene chloride/hexane). Based on our observations of various regions of the benzene-cast sample, we believe that, for the case of a casting

solvent which is good for both blocks, the mechanism of formation of the spherical morphology involves a path through the rod-like state (Figure 2) to a system of "unduloids" (rods whose diameters increase and decrease in a repeating pattern) and finally to spheres. Evidence of these unduloids appears in Figure 5 along with regions in which the unduloids have already "pinched-off" into spheres. The morphology of the toluene-cast sample shown in Figure 2 may also be interpreted as an early stage in this pinching-off process. Evidence for the formation of rod-like unduloids has been reported in the literature on low molecular weight liquids (26); interfacial tension is considered to be the critical parameter governing their formation and stability.

The most striking effect of the rate of solvent evaporation is the appearance of the large micron-scale islands in the background morphology as shown in Figure 3. In order to eliminate the possibility that something in the spin-casting process other than rate of evaporation led to these islands, spin castings were preformed in such a way that the solvent evaporation proceeded nearly as slowly as in the static slow-evaporation method. In these cases, no large islands were obtained and morphologies were essentially identical to those shown in Figure 2 for the various solvents used. Further evidence for the fact that the rate of evaporation controls the formation of the large islands is contained in the following observations: (i) Very rapid evaporation rates, as obtained in elevated temperature (ca 80° C) spin castings led to an increase in both the size and amount of the unstructured material. (ii) Some of the spin castings showed a gradient morphology in which the innermost material (i.e. the region of longest retention of solvent)

showed little or no evidence of the large unstructured islands whereas they appeared in large proportion in the outermost material.

We believe that the observed micron-sized regions appearing in four of the micrographs of Figure 3 consist of "homogenized" diblock copolymer which has not had enough time and mobility to undergo microphase separation to the more stable spherical morphology. The process of formation of these regions of homogenized diblock is represented qualitatively at the top of Figure 6. The process of evaporation of solvent from the ternary system of polyisoprene/poly n-butylmethacrylate/sovent proceeds along line A; at a certain concentration the binodal is reached and, if the process is slow enough, the system will split into two phases, following path B during the evaporation to dryness. If the rate of solvent evaporation is rapid, however, local regions of high viscosity may occur within the material at the binodal and these may not begin to phase separate as the binodal is crossed. Further evaporation of solvent decreases the mobility of the material still more, and locks these regions into the bulk film (path C). The absence of any regions of homogenized diblock in the spin cast sample prepared from methylene chloride/hexane (Figure 3) is attributed to the fact that preferential precipitation of the poly n-butylmethacrylate blocks occurs early in the casting process in this case, i.e. high in the ternary diagram where the mobility of the molecules in solution is still rather large.

If these large regions do represent homogenized diblock, they would be expected to be thermodynamically unstable (or perhaps metastable if they exist between the binodal and spinodal). Thus, it should be possible

given enough time, to observe their eventual decomposition to the more stable microphase-separated morphology. At room temperature in the bulk polymer we have not been able to observe this process. However, by increasing the mobility of the system, either by addition of solvent or by annealing for various periods of time at elevated temperatures, we have observed the postulated decomposition processs. The lower part of Figure 6 represents qualitatively the anticipated result of raising the temperature of the homogenized polymer assuming that the binary system of polyisoprene/poly n-butylmethacrylate shows a lower critical solution temperature (right) or upper critical solution temperature (left). In either case, raising the temperature increases the mobility of the homogenized regions and facilitates decomposition into two phases; this decomposition process may or may not proceed to the boundaries of the phase diagram, depending upon the amount of time allowed for the process to proceed.

The result of one such experiment is shown in Figure 7. For this case, a piece of the originally cast sample (Figure 3, benzene/pentanone) was held at 90° C for 24 hours in vacuo, then cooled, stained with OsO_4 and sectioned for microscopy. The resulting micrographs show clearly that the outer regions of the large islands are decomposed to the microphase morphology while the inner portions consist of concentric rings of isoprene lean and isoprene rich material. Depending upon the time and temperature, this decomposition process proceeded to varying degrees; however even after 120 hours at 90° C, the process was not complete. Addition of 70 wt% solvent appeared to allow the process to go to completion (based on a marked change from a turbid to a clear medium) but even in this case about 500 hours

were required.

The unusual morphologies exhibited by the polyisoprene/poly n-butylmethacrylate diblock may arise in part from the structure of the n-butylmethacrylate repeat unit. The polar groups in the ester moiety cause this methacrylate polymer to prefer polar solvents and to reject solvents of the nonpolar hydrocarbon variety; on the other hand, the n-butyl side group of this monomer is likely to have compatibilizing effect in the presence of hydrocarbons, including polyisoprene. In order to pursue these ideas further we are attempting to conduct experiments and to carry out calculations which will enable us to predict the form of the binary and ternary phase diagrams suggested in Figure 6, and to make quantitative estimates of the binodal and spinodal curves for the polyisoprene/poly n-butylmethacrylate system. Work is also in progress to determine whether physical properties are strongly affected by the size, shape and amount of homogenized diblock embedded in the microphase separated material and whether the extent of decomposition of these regions has an effect on properties.

Acknowledgements

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Table 1 Tabulated summary of pertinent characterization results.

Technique	cis 1-4 polyisoprene[a]	poly n-butyl methacrylate[b] (Made in Separate Homopolymerization)	cis 1-4 polyisoprene-b-poly n-butyl methacrylate
G.P.C.*	$\bar{M}_w/\bar{M}_N$ = 1.02	$\bar{M}_w/\bar{M}_N$ 1.1	$\bar{M}_w/\bar{M}_N$ = 1.1
Membrane Osmometry	$\bar{M}_N$ = 80000	$\bar{M}_N$ = 56,000	$\bar{M}_N$ = 243,000 (80,000-b-163,000)
DTA	-	-	T_g = -73° C T_g = 17° C
TMA	-	-	T_g = -69° C T_g = 16° C
Electron Microscopy	-	-	Two Phase Morphology Phase Morphology Solvent dependent

(a) Sample of isoprene polymer taken from reactor prior to addition of the second monomer.

(b) Low molecular weight n-butylmethacrylate homopolymer synthesized under conditions identical to those used for the second block of the diblock copolymer.

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FIGURE CAPTIONS

Figure 1 Gel permeation chromatography trace of homopolymers synthesized under conditions described in the text; GPC: Waters Model 244 10^6, 10^5, 10^4, 10^3 Å μ styrogel columns.

Figure 2 Morphologies of films obtained by slow solvent evaporation from solutions of the diblock copolymer in: (a) benzene/pentanone (b) benzene, (c) hexane/methylene chloride, (d) toluene, (e) methylene chloride.

Figure 3 Morphologies of films obtained by rapid spin casting from solutions of the diblock copolymer in: (a) benzene/pentanone (b) benzene, (c) methylene chloride, (d) hexane/methylene chloride

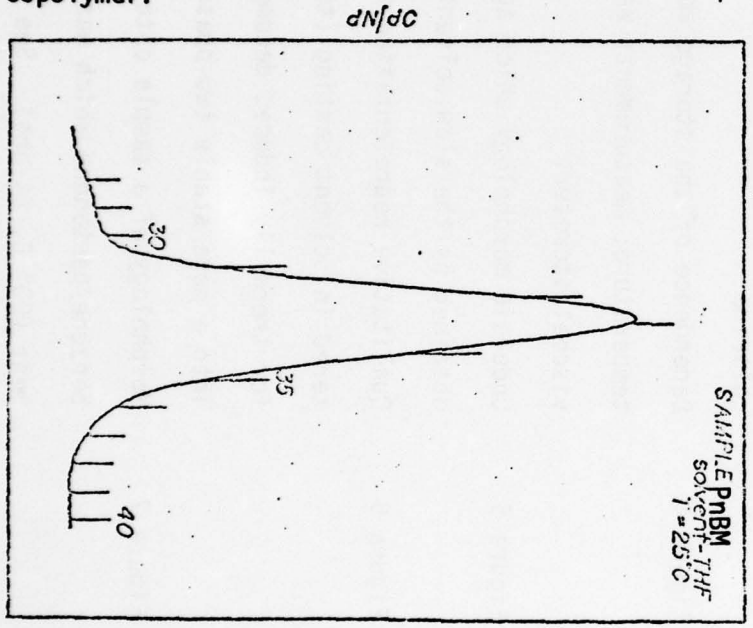
Figure 4 Dependence of the storage modulus and loss tangent on temperature; measurements were made at 3.5 Hz on a Rheovibron viscoelastometer.

Figure 5 Unduloid morphology which appeared in benzene cast samples obtained by the slow solvent evaportation method.

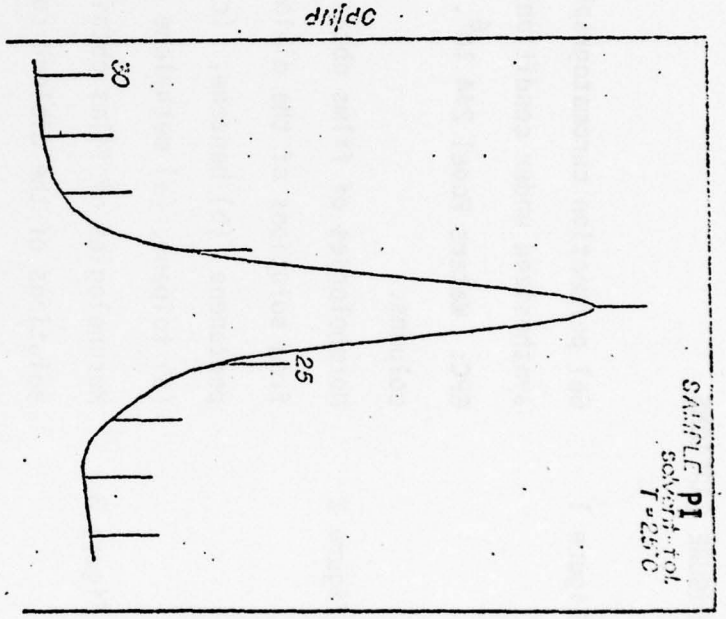
Figure 6 Qualitative representation of the various pathways encountered in solvent casting (top), and of the possibilities for thermally induced decomposition of homogenized diblock into a more stable two-phase structure (bottom).

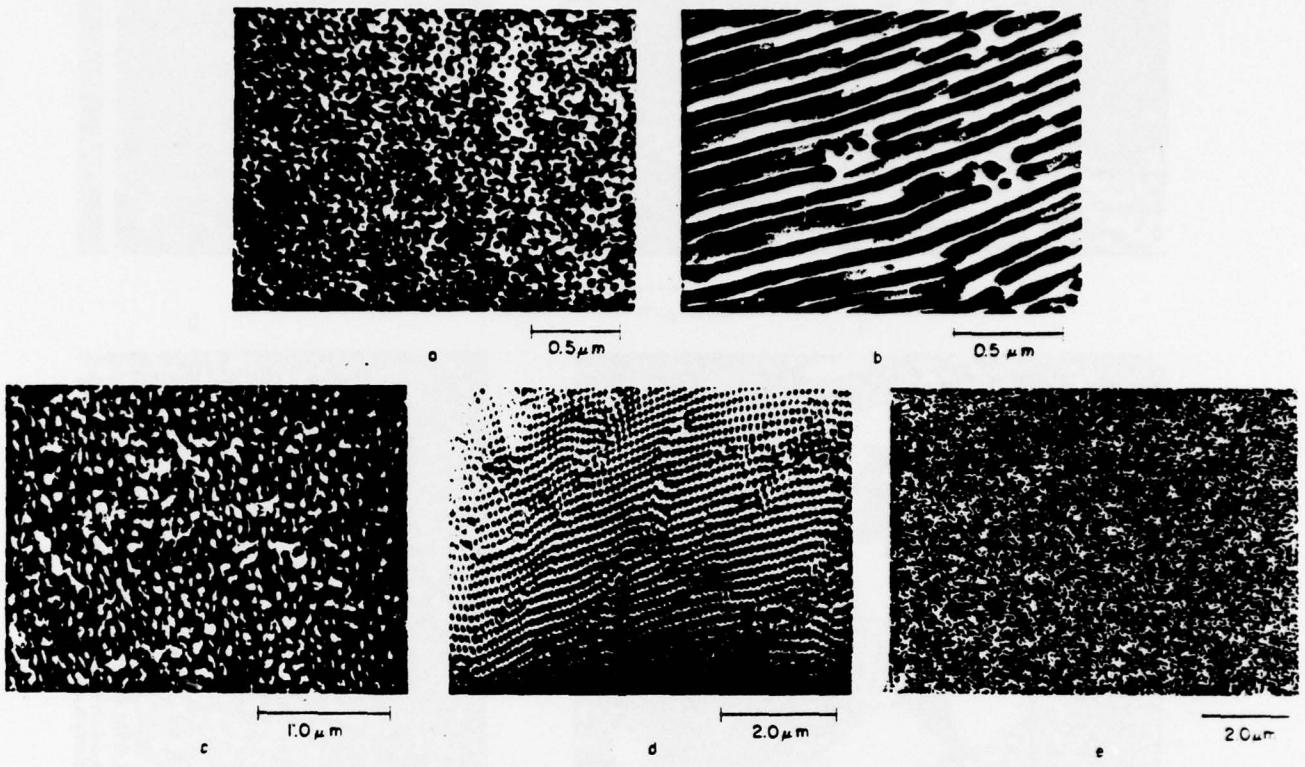
Figure 7 Morphology of a sample obtained by rapid spin casting from benzene/pentanone which was subjected to further heat treatment (90° C, 24 hrs). See Figure 3a for comparison with the morphology seen prior to heat treatment.

Poly n butylmethacrylate: Low molecular weight homopolymer synthesized under conditions identical to those used for the second block of the diblock copolymer.



Polyisoprene: Sample taken from the reactor prior to addition of the second monomer.

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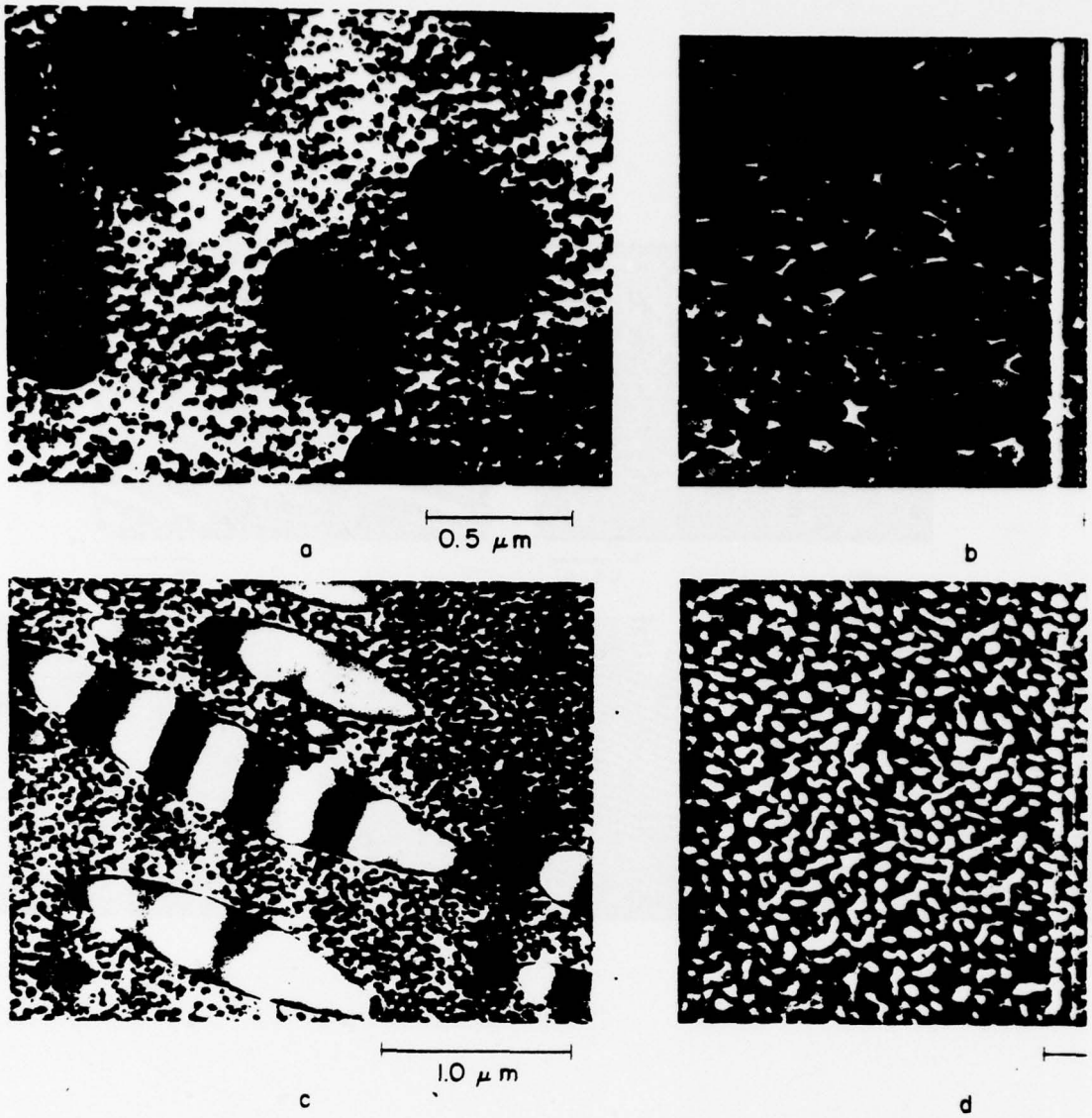
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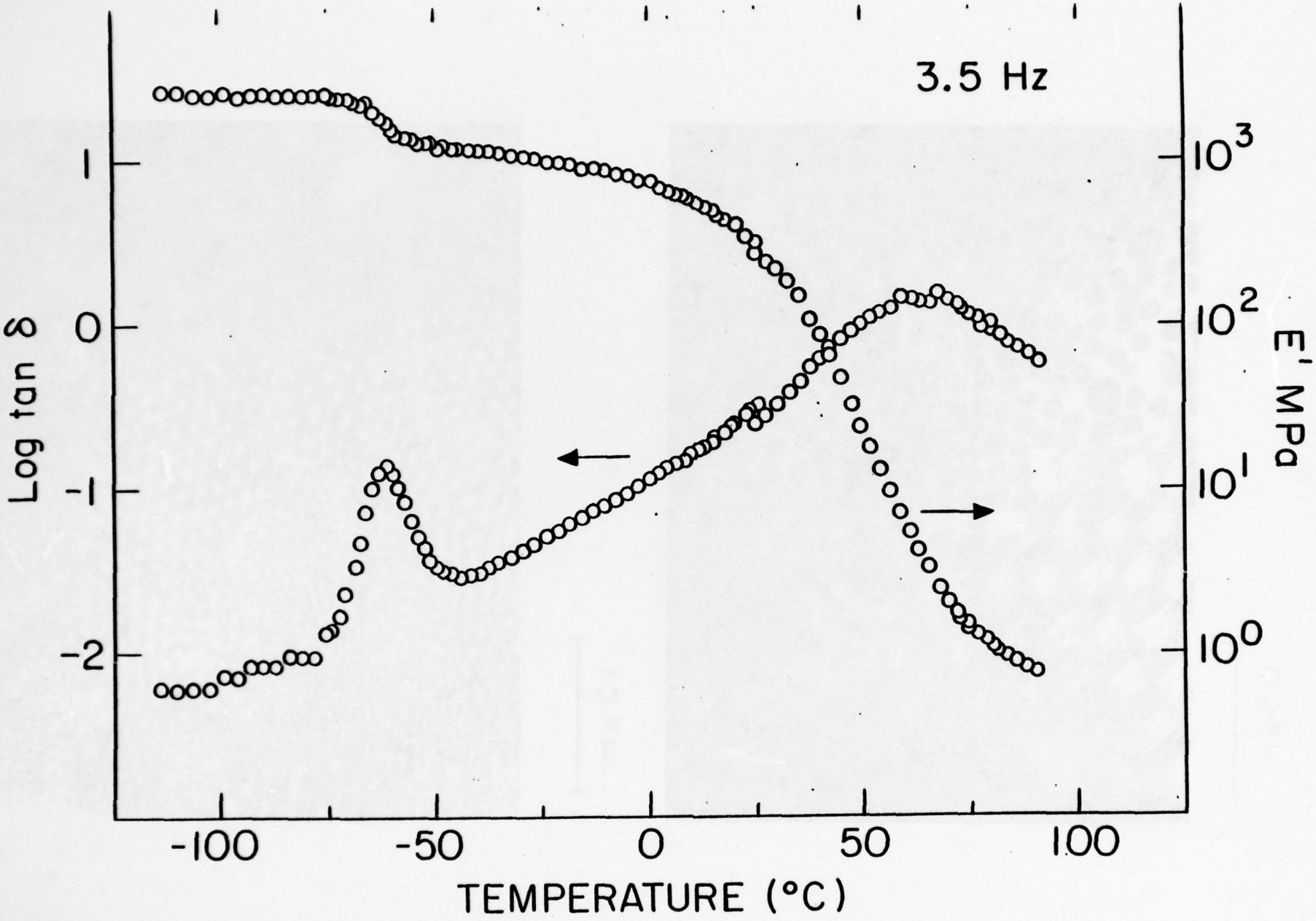
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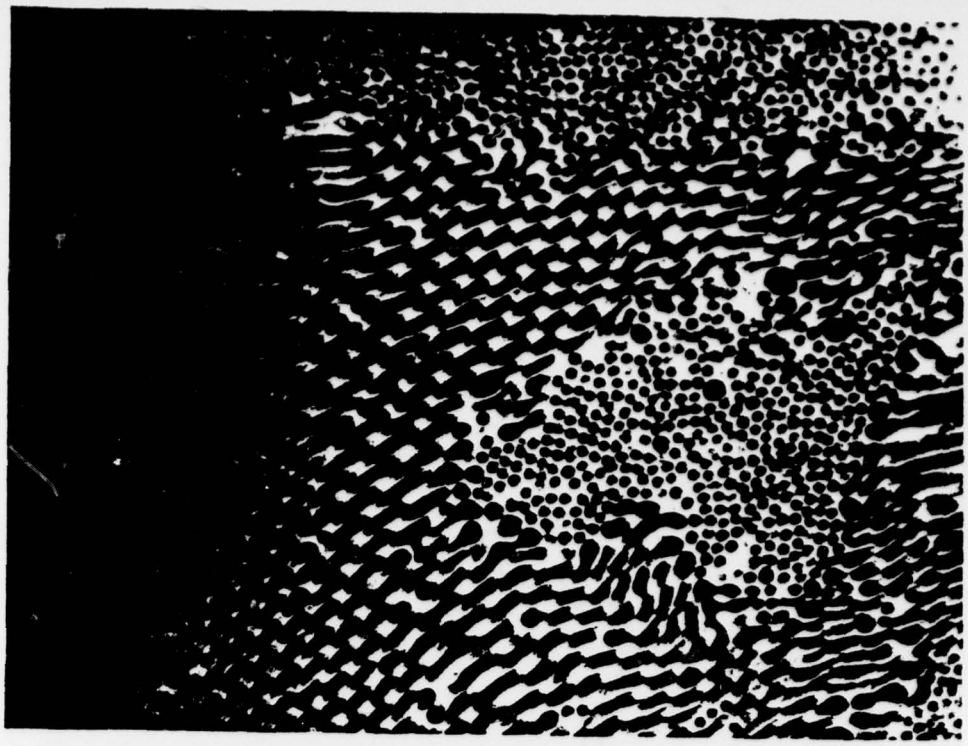

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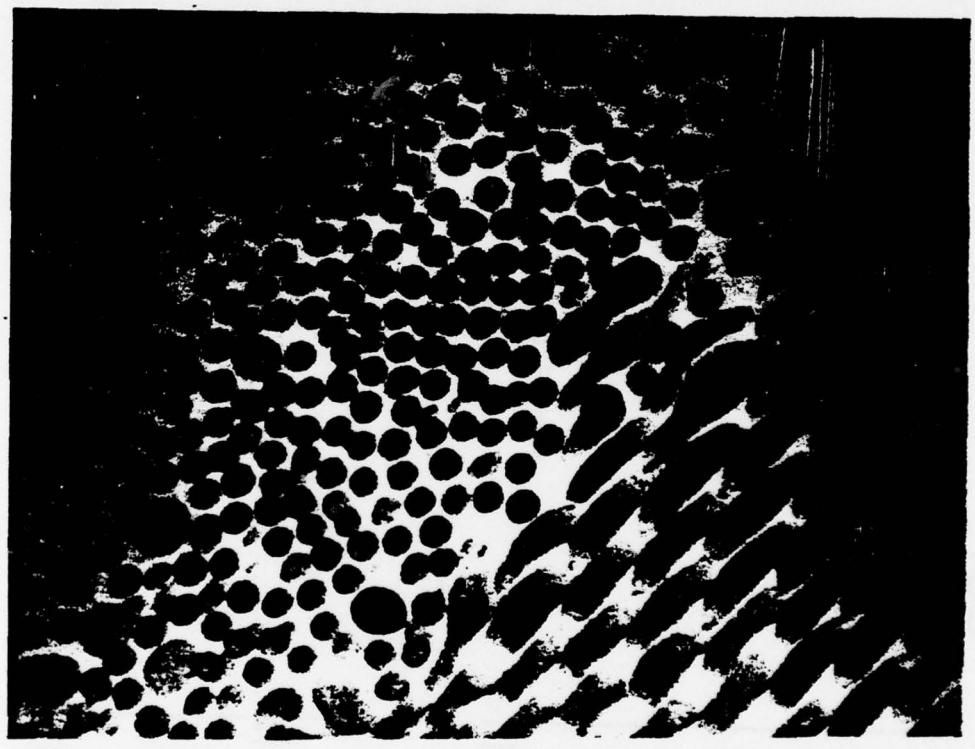
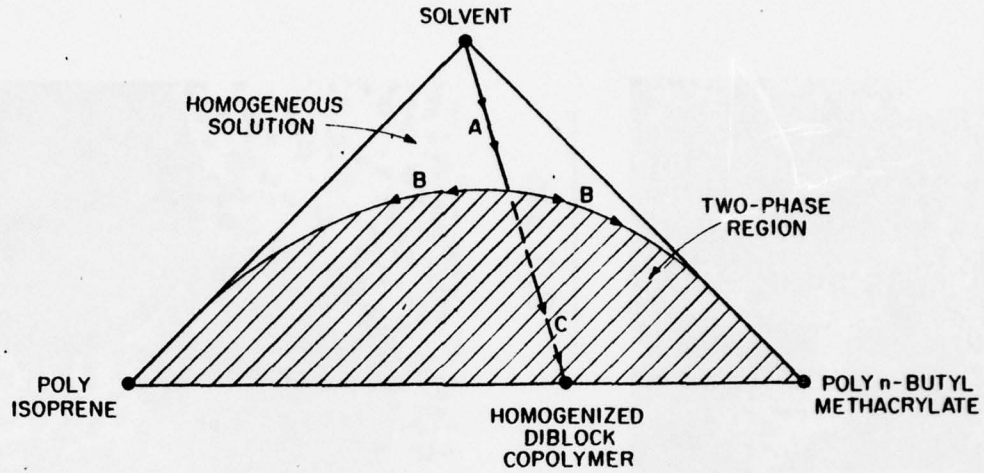
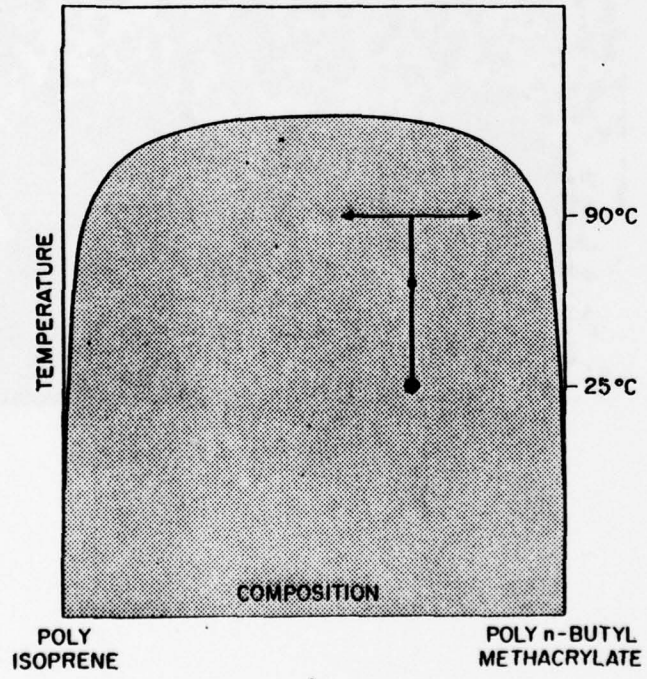


0.5 μm

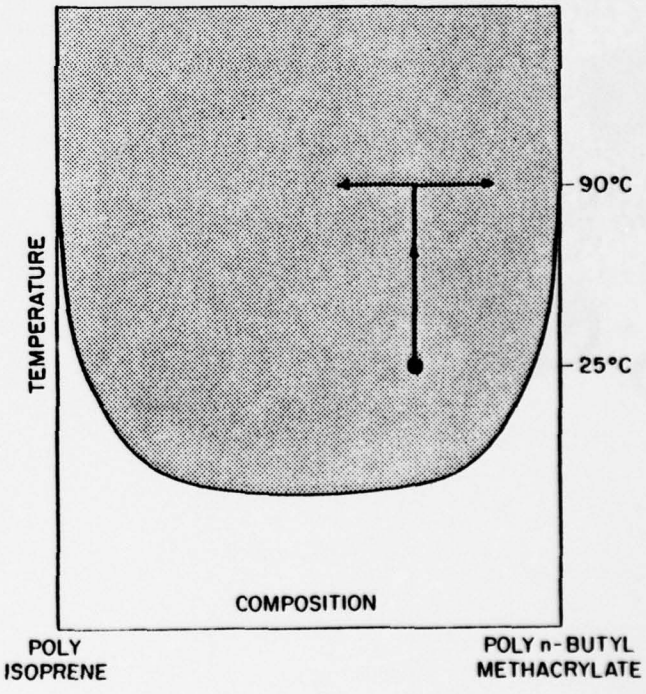
b


SOLVENT
HOMOGENEOUS SOLUTION
A
B
B
TWO-PHASE REGION
C
POLY ISOPRENE
POLY n-BUTYL METHACRYLATE
HOMOGENIZED DIBLOCK COPOLYMER

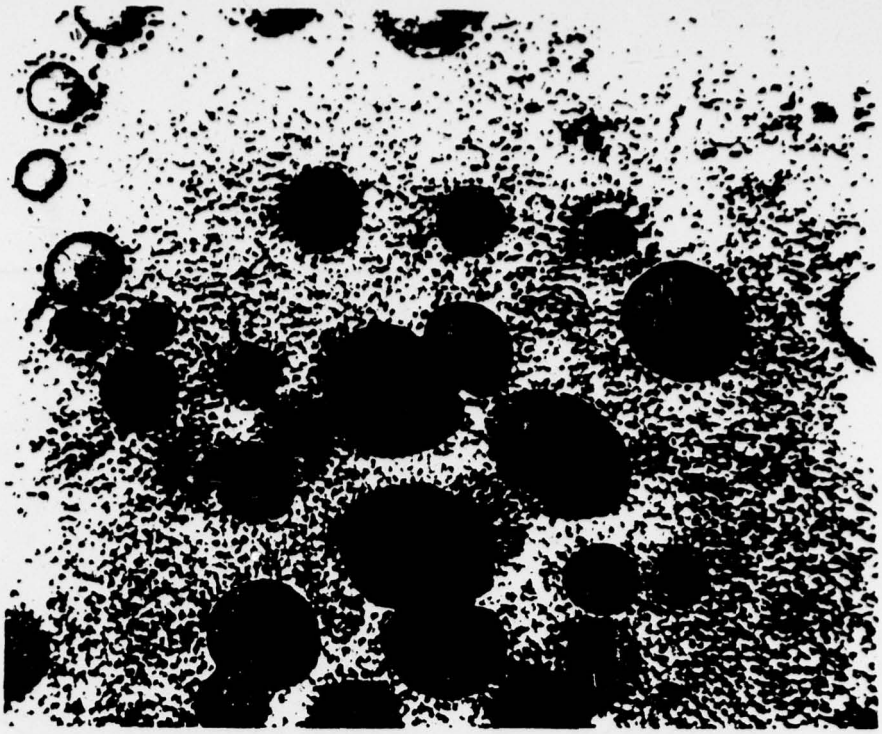
a


TEMPERATURE
90°C
25°C
COMPOSITION
POLY ISOPRENE
POLY n-BUTYL METHACRYLATE

b

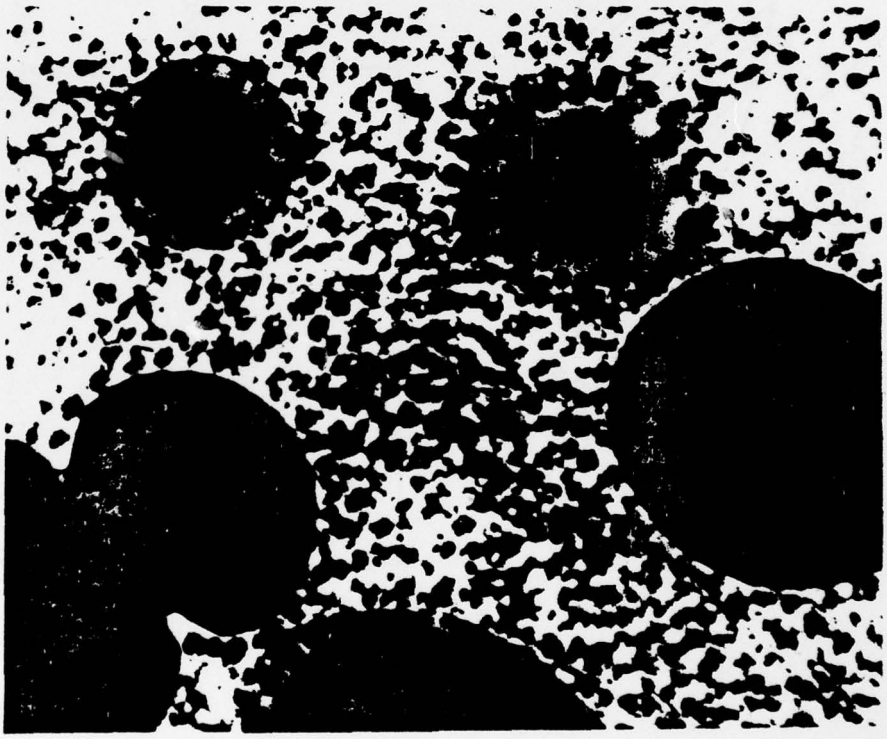

TEMPERATURE
90°C
25°C
COMPOSITION
POLY ISOPRENE
POLY n-BUTYL METHACRYLATE

c



2.0 μm

a



1.0 μm

b